



Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry

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ARTICLE INFO

Article history:

Received 14 June 2015

Received in revised form 21 August 2015

Accepted 23 August 2015

Available online 28 August 2015

Keywords:

Date palm

Pyrolysis temperature

Recalcitrant form

Volatile matter

Black carbon

ABSTRACT

The biochars (BC) were prepared from date palm waste to investigate the influence of pyrolysis temperature (300–800 °C) on composition and surface chemistry of BC. The results showed that fixed C, ash and basic cations of BC increased while its moisture, volatiles and elemental composition (O, H, N and S) decreased with increasing pyrolysis temperature. As the surface basicity of biochar increased by increasing pyrolysis temperature, the values of pH and pH_{pzc} were increased. The biochars produced at low pyrolysis temperature do possess some functional properties of their feedstock, whereas the aromatic functional units in biochar samples were condensed with increasing pyrolysis temperature. In this context, readily and potentially labile C oxidized using KMnO₄ and K₂Cr₂O₇ decreased with pyrolysis temperature, whereas recalcitrant C followed the opposite trend. Stronger correlations were found between volatile matter and O/C ($r^2 = 0.9971$) than those conducted between volatile matter and H/C ($r^2 = 0.9325$). Date palm-derived BC at ≥ 500 °C with a volatile matter less than 10% and O/C of 0.02–0.05, could be more appropriate for C sequestration. The BC may thus represent potential alternative materials for environmental management, depending upon pyrolysis temperature.

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1. Introduction

Biochar is a solid product produced from thermal conversion of unstable carbon-enriched materials into stable carbon-enriched charred materials that can be incorporated into the soils as a mean for agronomic or environmental management [1]. The incorporation of biochar into soil has been reported to be an efficient technique to mitigate greenhouse gas emissions [2]. Biochar application in enhancing soil properties and fertility as well as remediation of contaminated soil has been also reported by several researchers [3–5]. Several other researchers have also found that biochars can be used as alternative sorbents to remove different types of organic and inorganic contaminants from aqueous solutions [6,7]. However, its effects on long-term carbon sequestration,

soil fertility, and environmental remediation are mainly dependent upon physicochemical properties of biochar [8,9].

Pyrolysis temperature and feedstock type are considered to be the main factors affecting quality and controlling properties of biochar [5,10,11]. Among them, pyrolysis temperature is the key factor affecting the formation and volatilization of intermediate compounds [12]. It is important to note that pyrolysis temperature results in volatilizing some elements such as N and S, but it can cause other elements such as C to concentrate in the yielded biochar [13]. Pyrolysis temperature has direct influence on the elements being potentially lost to the atmosphere, fixed into more stable fractions or released as soluble forms during the pyrolysis process [14,15]. Biochar produced at high pyrolysis temperature possess a high pH value and liming effects as well as utmost specific surface area [10]. Therefore, comparing the differences between biochar properties in relation with pyrolysis temperature is needed in order to determine the effect of pyrolysis temperature on composition and surface chemistry of biochars, reflecting on agronomic and environmental management.

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Due to their low cost, converting of agricultural wastes into biochars has potential for reducing solid wastes disposal problem. Date palm is one of the highly cultivated palms in Saudi Arabia, constituting more than 22 million trees. The generated huge amounts of date palm wastes is either buried in landfills or burned directly in open fields causing serious threat to the environment and human health. To our knowledge, there is no research to date on the production and characterization of biochar produced from date palm waste along a wide range of pyrolysis temperature in literature. Therefore, the aim of this work is to investigate the effect of pyrolysis temperature on date palm derived biochar characteristics related to its composition and surface chemistry to evaluate its suitability for agronomic or environmental management.

2. Materials and method

2.1. Date palm waste pyrolysis

Date palm tree waste including leaves, branches and stem barks was collected from Riyadh city, Saudi Arabia. The waste was dried in air under sunshine and then chopped to small pieces. Pyrolysis of the processed date palm waste was carried out in a closed stainless steel container (22 cm in height and 7 cm in diameter) using an electrical muffle furnace. Different temperatures of 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C were maintained for 4 h under a limited supply of air to obtain different biochars. Feedstock samples were pyrolyzed to the desired temperature at the rate of 5 °C min⁻¹. The biochars produced at different charring temperatures (300–800 °C) were left to cool inside the furnace overnight. The produced biochars are named as BC300, BC400, BC500, BC600, BC700 and BC800, where BC and numbers denoting biochar and pyrolysis temperatures, respectively.

2.2. Yield and proximate analyses of biochar

Proximate analyses including moisture, ash, and volatile matter in biochar were determined according to ASTM D1762-84 standard method [16]. The resident matter (fixed carbon) was calculated by subtracting the contents of ash, volatiles matter and moisture from 100.

2.3. Ultimate analyses and elemental molar ratios of biochar

The total elemental content of C, H, N, and S in biochar samples were measured by CHNS analyzer (series II, PerkinElmer, USA). The percentage of oxygen content was calculated by the following equation:

$$O(\%) = 100 - (C + H + N + S + \text{ash}, \%)$$

The atomic ratios of H/C, O/C, O+N/C, and O+N+S/C were also calculated as indicative of aromaticity and polarity. Moreover, biochar samples were analyzed for soluble and total elemental content of basic cations (Ca, Mg, Na and K). Soluble Ca, Mg, Na and K were measured in an aqueous extract (1:25). However, their total elemental contents were measured after wet digestion using HNO₃ [17]. The total and soluble contents of Na and K of each extract were determined by using flame photometer, whereas the total and soluble contents of Ca and Mg were determined by inductively coupled plasma optical emission (ICP-OES) spectrometer (Perkin Elmer Optima 4300 DV ICP-OES).

2.4. pH, EC and potentiometric titration

Biochar pH and electrical conductivity (EC) were measured in a suspension and an aqueous extract of biochar-to-water ratio of

1:25 with pH and EC meters, respectively. The ΔpH values were estimated after biochar pH measuring in a suspension of biochar-to-KCl ratio of 1:25 and calculated using following equation:

$$\Delta\text{pH} = \text{pH}(\text{biochar to KCl ratio of } 1 : 25) \\ - \text{pH}(\text{biochar to water ratio of } 1 : 25)$$

Changes in the pH value of biochar samples after increasing addition of HCl or NaOH were determined [18]. The acidic and basic functional groups were determined by titration with basic solutions (NaHCO₃, Na₂CO₃, and NaOH) or acid (HCl) solution, according to Boehm method [19].

To characterize zero net charge and amphoteric surfaces of biochars, the pH of point zero charge (pH_{pzc}) was also estimated. Specifically, biochar samples (0.5 g) with 50 mL of NaCl solution (0.10 mol L⁻¹) were adjusted by adding a small amount of diluted HCl or NaOH solution and then, initial pH values were measured. The final pH was then measured after 24 h of shaking at room temperature. The pH_{pzc} values of the date palm biochar samples were estimated by plotting the pH_{initial} against the pH_{final} [20].

2.5. Biochar carbon forms

Readily labile organic carbon of biochar was determined by oxidation using 333 mM KMnO₄ followed by measuring absorbance at 565 nm using UV/visible spectrophotometer (Lambda EZ150, Perkin Elmer) [21]. The potentially unstable organic carbon (C_{org}) was determined by oxidation using 0.167 M K₂Cr₂O₇ followed by titration with 0.5 M Fe(NH₄)₂SO₄ [22]. Stable/recalcitrant carbon was calculated by the differences between the total carbon measured by CHN analyzer and the potentially unstable organic carbon (C_{org}) contents of the biochar samples.

2.6. SEM, TG, FTIR and XRD analyses of biochars

To identify the changes in the biochar surface structure during pyrolytic process, scanning electron microscope (SEM) (FEI, Inspect S50) imaging analyses of biochar samples were carried out. The thermal changes in biochar weight were evaluated by using the thermo-gravimetric (TG) analyses. To characterize the whole composition of functional groups of feedstock and biochar samples, the fourier transformation infrared (FTIR) analysis was carried out using FTIR spectrometer (Nicolet 6700 FTIR). The X-ray diffraction (XRD-7000 Shimadzu) analysis of biochar samples was also conducted to determine the mineralogical phases.

3. Results and discussion

3.1. Yield and proximate composition of date palm biochars

The results showed that highest yield of biochar was achieved at the lowest pyrolysis temperature (300 °C) (Table 1), owing to less aliphatic fractions concentration and minimum loss of O- and H-containing surface functional groups. The biochar yield was about 50.0% at the lowest pyrolysis temperature but it decreased to <29.0% as the pyrolysis temperature was increased up to 700 °C. This reduction in biochar yield with increasing pyrolysis temperatures has been reported to be mainly due to thermal degradation of cellulose and hemicellulose as well as dehydration of hydroxyl groups [23].

As a consequence of the pyrolytic process, the fixed C and ash contents of the biochars were concentrated (Table 1). On the contrary, the moisture and volatiles contents decreased with increasing temperature. Compared to the feedstock (22.3%), biochars possess a higher content of fixed carbon (45.49–74.70%).

Table 1

Effect of pyrolysis temperatures on yield, proximate composition analysis, elemental composition and the atomic ratios of biochar.

Parameters	Feedstock	Pyrolysis temperature (°C)					
		300	400	500	600	700	800
Yield and proximate composition analysis (Percentage recovery)							
Yield	–	49.97	36.54	32.38	30.88	28.84	27.40
Ash	7.11	14.42	16.34	19.68	20.71	21.05	21.39
Fixed C	22.30	45.49	63.41	71.00	72.44	73.49	74.70
Volatiles	70.59	40.08	20.25	9.31	6.85	5.47	3.91
Moisture	7.60	3.29	3.13	2.96	2.25	2.12	2.09
Elemental composition (% oven-dry wt. basis)							
C	43.19	57.99	66.87	72.30	72.89	73.42	74.63
H	5.83	4.08	3.54	2.11	1.74	1.14	0.86
O	39.00	20.82	11.44	4.50	3.28	3.19	2.27
N	0.70	0.54	0.45	0.42	0.39	0.35	0.31
S	4.16	2.14	1.36	1.02	0.98	0.85	0.54
Ca	2.53	4.85	6.04	5.81	7.77	7.65	8.08
Mg	0.68	1.53	1.57	1.93	1.90	1.92	2.02
K	1.32	2.18	2.17	2.23	2.58	2.69	2.71
Na	0.28	0.40	0.42	0.48	0.53	0.50	0.58
Molar ratios							
O/C	0.68	0.27	0.13	0.05	0.03	0.03	0.02
H/C	1.61	0.84	0.63	0.35	0.28	0.19	0.14
(O + N)/C	0.69	0.28	0.13	0.05	0.04	0.04	0.03
(O + N + S)/C	0.73	0.29	0.14	0.06	0.04	0.04	0.03
C _{org} /N	71.69	68.01	51.65	32.24	23.36	19.04	18.03

In addition, the ash contents of feedstock and its derived biochars ranged from 7.1 to 21.4%. The highest percentage of ash was found in BC800. The results are consistent with several other researchers explaining an increase in ash percentage with increasing pyrolysis temperature owing to the formation of mineral compounds and/or condensation of mineral elements in biochar during pyrolytic process [5,24,25].

It has been hypothesized that the volatile matter content is an index to predict the stability of biochar, assuming high stability with low volatile matter [26,27]. However, Spokas [28] reported that O/C ratios were better correlated with biochar stability than its volatiles. In this study, correlation analysis between volatile matter and O/C, H/C, O/C_{org}, or H/C_{org} was conducted to distinguish the stability of date palm biochars with temperature (Fig. 1). The results showed that there are better and stronger relation between volatile matter and O/C ($r^2=0.9971$) than those conducted between volatile matter and H/C ($r^2=0.9325$), or O/C_{org} ($r^2=0.5853$), or H/C_{org} ($r^2=0.7138$). In literature, biochars with a half-life of 100–1000 years have an O/C of 0.2–0.6, but biochars with a half-life of greater than 1000 years possess an O/C of less than 0.20 [28]. Based on this report, the obtained results suggest that date palm biochars with a volatile matter less than 10% and with O/C of 0.02–0.05, which was occurred at pyrolysis temperature $\geq 500^\circ\text{C}$, presumably possessing a high C sequestration potential.

3.2. Biochar elemental composition and molar ratios

The results showed that the biochar H, O, N and S contents decreased with increasing temperature (Table 1). These declines can be due to the pyrolytic process, resulting in loss of O- and H-containing surface functional groups by dehydration [9,11]. In addition, the possible volatilization of S and N through the pyrolytic process can cause the decline in their total content. On the contrary, the total content of C increased with increasing pyrolysis temperature from 43.19% in feedstock to 57.99–74.63% in biochar samples. The increase in the biochar C content could be due to the increased carbonization degree [10]. There were significant impacts of pyrolysis temperature on total content of basic cations (Ca, Mg, K and Na). The maximum total content of basic cations was observed in biochars produced at highest temperature of 800°C . Increase in

total contents of basic cations with pyrolysis temperature could be attributed to enrichment of biochar with inorganic basic minerals in the form of high ash contents.

The elemental composition of feedstock and biochars was used to calculate atomic ratios to predict polarity and potential interaction with water. The results showed that feedstock possesses higher molar ratios of O/C, H/C, (O+N)/C, and (O+N+S)/C than those of biochars (Table 1). Among biochars, these ratios decreased with increasing pyrolysis temperature. The molar O/C and H/C ratios of biochars ranged between 0.02–0.27 and 0.14–0.84, respectively. The decline in the O/C and H/C ratios with increasing pyrolysis temperature is in relation with the degree of aromaticity and maturation, indicating increasing the degree of aromaticity with increasing pyrolysis temperature [9]. Among different BCs, the highest H/C ratio (0.84) was pronounced for BC300. The low H/C presented more hydrophobic nature of BCs produced at $\geq 500^\circ\text{C}$ relating their low affinity with water. The lowest ratio of the (O+N)/C at higher temperature suggests lower polar functional groups and higher aromaticity than those of biochar produced at lower temperature, especially at lowest one (BC300). As the pyrolysis temperature increased, C_{org}/N ratio decreased and the lowest ratio was found at 800°C . The decline in C_{org}/N ratio during pyrolysis could be as a result of the depletion of organic carbon. The results showed the decline rate in C_{org} was greater than total nitrogen decline rate, resulting in a lower C_{org}/N ratio. It has been reported that the high elemental molar ratios for the biochars pyrolyzed at lower temperature indicate an incomplete thermal conversion of unstable carbon-enriched materials into stable carbon-enriched charred materials [29].

As indicated by van Krevelen plot, the continued decrease in the H/C and O/C atomic ratios with pyrolysis temperature was in relation with dehydration reactions (Fig. 2), suggesting the lower the ratio the higher degree of aromaticity and stability with increasing pyrolysis temperature [30]. The high loss of H and O pronounced for biochar produced at the pyrolysis temperature of $500\text{--}800^\circ\text{C}$ with molar H/C ratio of <0.6 and molar O/C ratio of <0.4 , being considered to have biochar characteristics. Moreover, the biochars produced at $\geq 700^\circ\text{C}$ may do possess soot-like/graphitic BC characteristics.

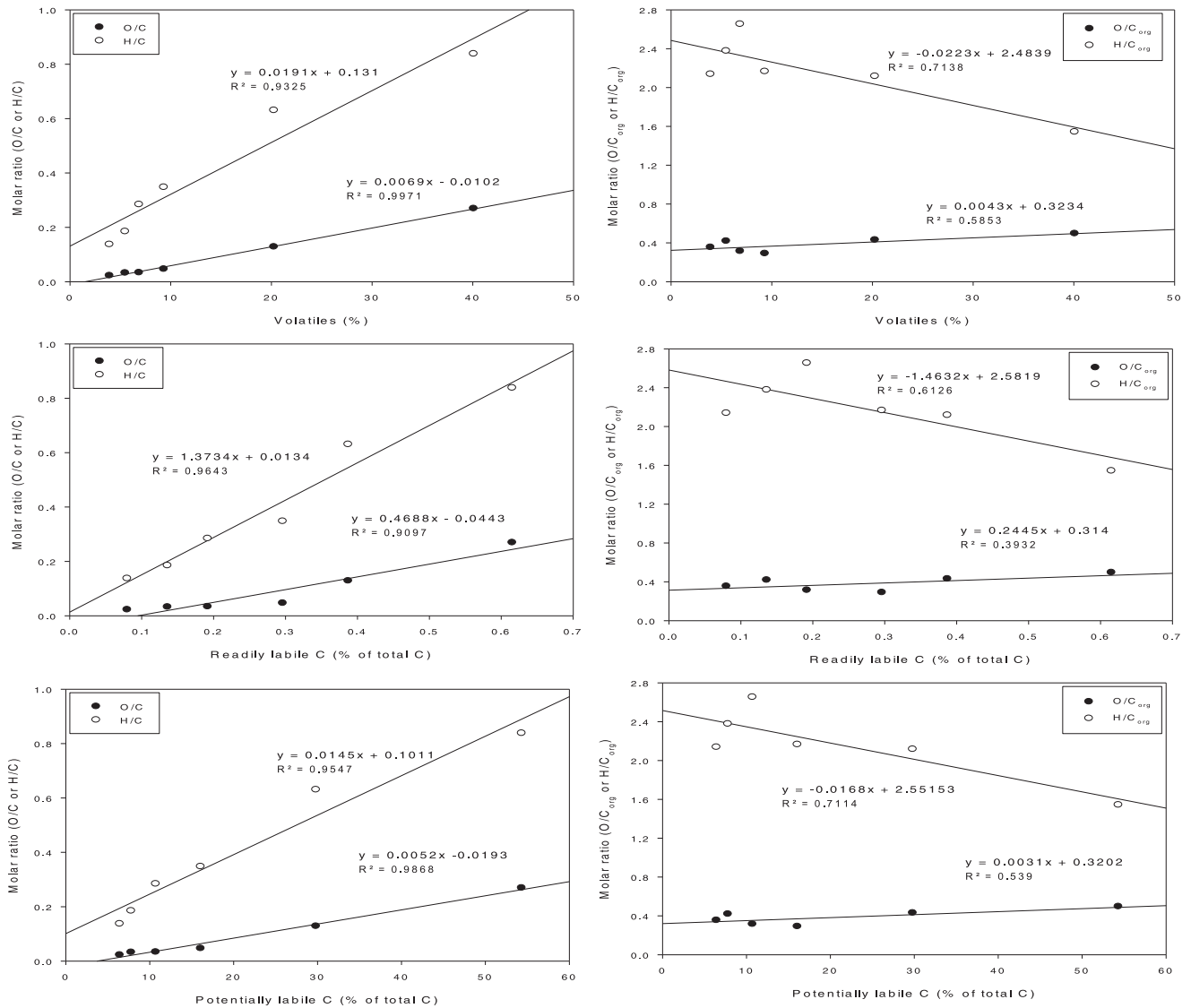


Fig. 1. Correlations between volatile matter and O/C, H/C, O/C_{org}, or H/C_{org}.

3.3. Labile and recalcitrant forms of biochar carbon

It has been reported that $K_2Cr_2O_7$ and $KMnO_4$ could be used to determine readily labile and potentially unstable organic C fractions, as these reagents are not able to react with the recalcitrant carbon of biochar [31]. Obviously, the results on the carbon oxidized by $KMnO_4$ (readily labile C) or $K_2Cr_2O_7$ (potentially

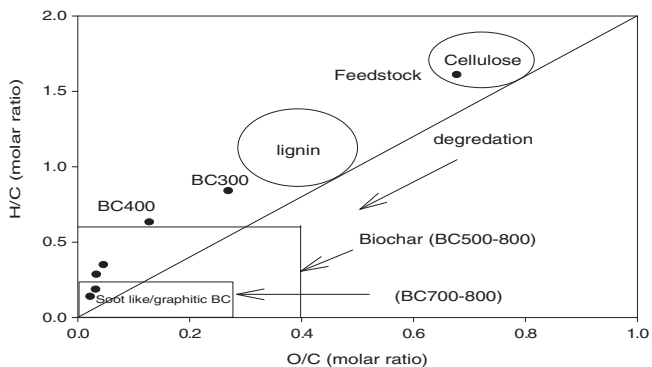


Fig. 2. van Krevelen plot of elemental ratios for date palm and its derivative biochars.

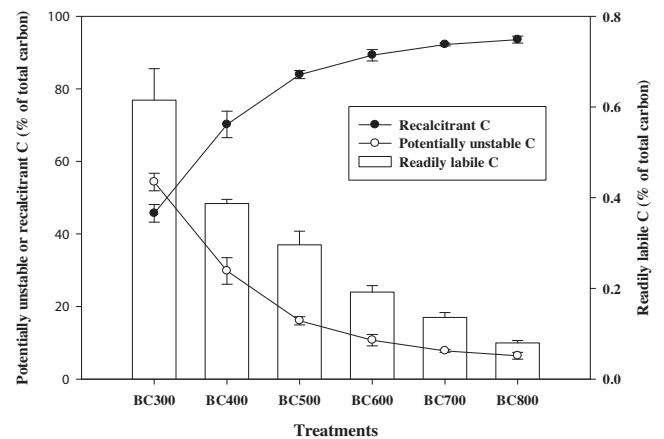


Fig. 3. Labile and recalcitrant form of biochar carbon as affected by pyrolysis temperature.

unstable carbon, C_{org}) in biochar samples indicated that oxidizable carbon by using $KMnO_4$ was less than that oxidized using $K_2Cr_2O_7$ (Fig. 3). Generally, it was observed that both $KMnO_4$ -

and $K_2Cr_2O_7$ -oxidisable C decreased as pyrolysis temperature increased, whereas C in the recalcitrant form showed the opposite trend. The potentially unstable organic carbon oxidized by $K_2Cr_2O_7$ for BC300 accounts for 54.3% of total biochar carbon, which is higher than that of the recalcitrant biochar carbon accounting for 45.7%. However, this percentage of potentially unstable organic carbon (C_{org}) decreased with increasing pyrolysis temperature and reached to 6.4% for BC800. Meanwhile, the percentage of the recalcitrant biochar carbon became higher than that of C_{org} when pyrolysis temperature progressed and increased to 93.6% of total carbon in biochars pyrolyzed at highest temperature of 800 °C, suggesting a more aromatic biochar with increasing the pyrolysis temperature [31].

The relationships between the readily labile or unstable biochar C and H/C or O/C atomic ratios were evaluated (Fig. 1). The H/C or O/C atomic ratios showed a positive significant correlation with the readily labile or potentially unstable biochar C (oxidized using $KMnO_4$ or $K_2Cr_2O_7$, respectively). The strong positive and significant correlations with $r^2 = 0.9868$ were found between O/C and the potentially unstable carbon (C_{org}). Our result suggests that the oxidation using $KMnO_4$ and/or $K_2Cr_2O_7$ can be used to estimate the carbonization degree of materials in addition to labile or potentially unstable biochar C in biochar.

3.4. Biochar pH, potentiometric titration, and acidic and basic functional groups

The results showed that the feedstock exhibited a pH of 7.42 (in 1:25 ratio of biochar to water). However, this value was ~1 unit lower (6.50) when measured in 1:25 ratio of feedstock to 1 M KCl (Table 2). The pH values of produced biochars ranged between 8.32 and 11.50 in water suspension and between 8.16 and 11.72 in KCl suspension, indicating an alkaline nature. It was generally observed that the pH of 300 °C biochar was much lower, compared to 400–800 °C biochars, especially with increasing pyrolysis temperature. These increases with charring temperature are mainly due to liming induced by decreasing acidic functional groups and subsequently, increasing basic functional groups as well as alkali salts separating from organic compounds [32]. The data of ΔpH suggests that feedstock and BC300 samples possess net negative surface charge, but BC400–BC800 samples have net positive surface charge.

In addition, titration curves representing the pH changes after acid and alkali addition were carried out (Fig. 4). The results showed clear differences in acid neutralizing ability of different produced biochars (Fig. 4). A higher buffering capacity was found with increasing pyrolysis temperature, mainly due to the forma-

tion of the basic functional groups. The pH values of the produced biochars ranged from 8.32 to 11.62, which is in line with those in literature that generally biochars are alkaline [10,33]. The points of zero charge of biochars at different temperatures are shown in Fig. 5b. The pH_{pzc} of the produced biochars accounted for 3.8 for feedstock, 7.4 for BC300, 9.2 for BC400, 9.9 for BC500, 10.2 for BC600, and 11.3 for BC700 or BC800. As the surface basicity of biochar increased by increasing pyrolysis temperature, the values of pH and pH_{pzc} were increased, whereas pyrolysis temperature of 300 °C caused the lower values. It was generally observed that the decrease or increase in the values of pH and pH_{pzc} are strongly related with the acidic and basic functional groups of biochar.

The changes of acidic and basic functional groups of biochar are presented in Fig. 5. The content of total surface acidic functional groups ranged from 0.23 to 3.05 mmol g⁻¹, carboxylic groups ranged from 0.05 to 1.70 mmol g⁻¹, phenolic groups ranged from 0.16 to 1.07 mmol g⁻¹, and lactonic groups ranged from N.D. to 0.28 mmol g⁻¹ (Fig. 5b). The results showed that more total surface acidic functional groups were pronounced for the date palm feedstock than those of biochar samples (Fig. 5a). Generally, the content of surface acidic functional groups decreased as pyrolysis temperature increased, indicating the aliphatic transformation into aromatic moieties. On the contrary, the content of total basic functional groups followed the opposite pattern. Similar to this study, some researchers found an advanced loss of acidic surface functional groups with increasing charring pyrolysis temperature, but the total surface basicity increased with temperature [11,32]. Generally, the obtained data of surface acidic and basic groups are in line with the increased pH values of biochars when pyrolysis temperature increased. The obtained data of acidic functional groups of biochars are also consistent with the decreased volatile matter, potentially unstable carbon (C_{org} , $K_2Cr_2O_7$ -oxidizable carbon) and readily labile form of C ($KMnO_4$ -oxidizable C) in biochars when pyrolysis temperature increased. The obtained strong correlation between total acid functional groups and volatile matter or $K_2Cr_2O_7$ -oxidizable carbon ($R^2 = 0.96$ and 0.97, respectively) indicates that the higher volatile and organic matter of 300 °C biochar is responsible for the higher acidic functional groups at lower pyrolysis temperature. It has been suggested that volatile organic matter is not easy to be lost at pyrolysis temperature of lower than 400 °C and can be altered with charring in the range of 400–600 °C [32].

3.5. Biochar EC and soluble basic cations

There were significant impacts of pyrolysis temperature on electrical conductivity (EC) and soluble content of basic cations (Table 2 and Fig. S1). The results showed that the EC values tended to increase with increasing pyrolysis temperature. For soluble basic cations, the soluble Ca decreased from 189 mmol kg⁻¹ in feedstock to 136–179 mmol kg⁻¹ for biochar pyrolyzed at ≤ 700 °C. However, these values increased to be higher (230 mmol kg⁻¹) than those of feedstock (189 mmol kg⁻¹) when biochar pyrolyzed at 800 °C. This could likely be related to calcination of less soluble $CaCO_3$ to more soluble CaO at 800 °C (Fig. 6a). The soluble concentrations of Mg, however, tended to decrease with pyrolysis temperature and reached to minimal concentrations at the highest two pyrolysis temperatures. This can be explained by possible conversion of soluble Mg form into insoluble inorganic compounds by forming minerals as indicated by the obtained data from XRD, which suggests the formation of periclase (MgO) at high pyrolysis temperature (Fig. 6a). For soluble K and Na, their concentrations increased up to pyrolysis temperature of 500 °C and then, only for Na, showed a reduction with increasing pyrolysis temperature. However, soluble K remained relatively constant above pyrolysis temperature of 500 °C. Our results suggest that pyrolysis temperature has direct influence on the basic cations being potentially enriched, released

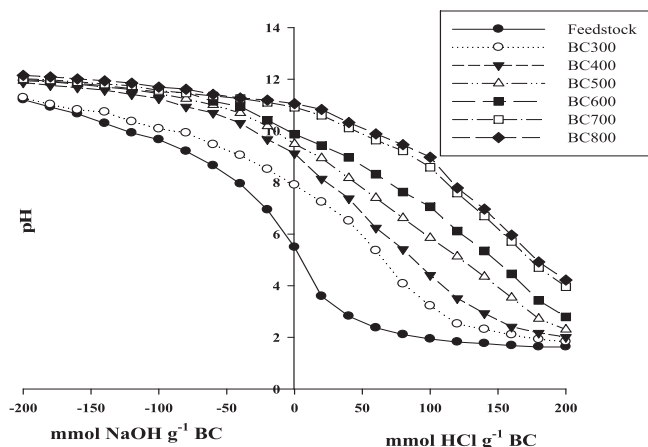
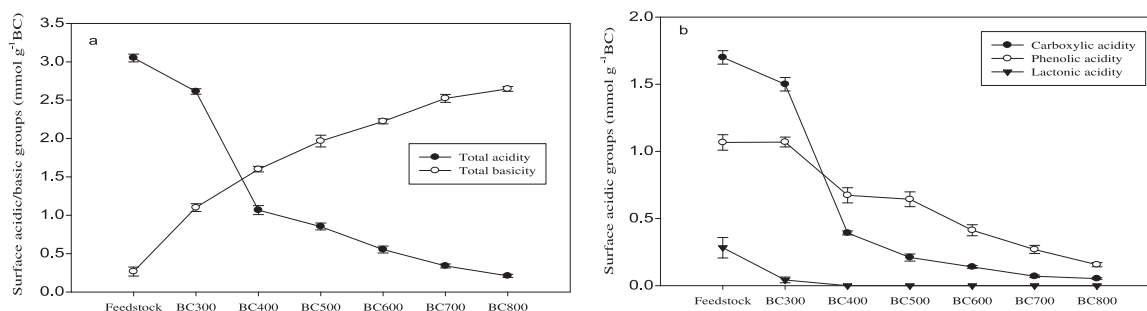
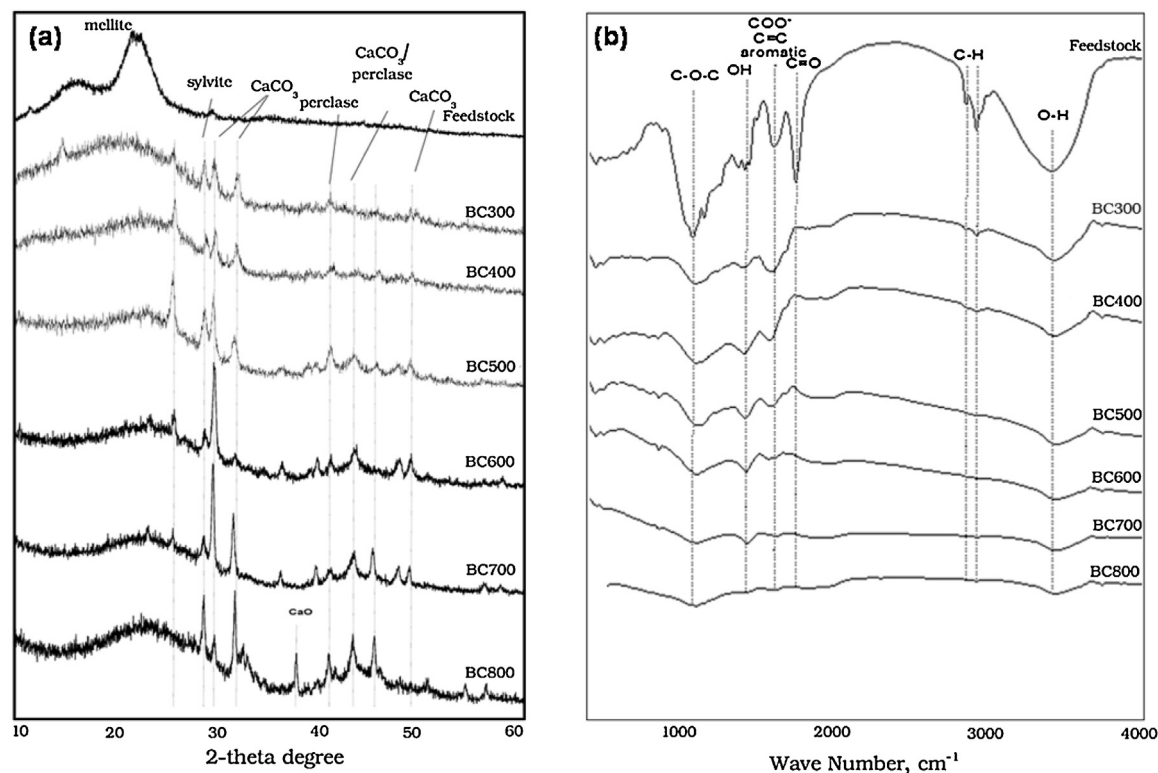


Fig. 4. Titration curves for date palm biochars.

Table 2Effect of pyrolysis temperatures on pH, EC and Δ pH of biochar derived from date palm wastes. Average of three replicates $\pm$ standard deviation is reported.

Samples	EC (dS m ⁻¹)	pH _{1:25} (Water)	pH _{1:25} (KCl)	Δ pH	pH _{pzc}
Feedstock	2.83 $\pm$ 0.11	7.42 $\pm$ 0.03	6.50 $\pm$ 0.28	-0.92 $\pm$ 0.25	3.8 $\pm$ 0.04
BC300	3.26 $\pm$ 0.30	8.32 $\pm$ 0.12	8.16 $\pm$ 0.16	-0.16 $\pm$ 0.04	7.4 $\pm$ 0.06
BC400	3.28 $\pm$ 0.26	9.25 $\pm$ 0.14	9.545 $\pm$ 0.16	0.30 $\pm$ 0.02	9.2 $\pm$ 0.05
BC500	3.50 $\pm$ 0.01	9.59 $\pm$ 0.01	9.80 $\pm$ 0.08	0.21 $\pm$ 0.07	9.9 $\pm$ 0.08
BC600	3.59 $\pm$ 0.03	9.57 $\pm$ 0.16	10.08 $\pm$ 0.03	0.52 $\pm$ 0.13	10.2 $\pm$ 0.06
BC700	3.66 $\pm$ 0.01	11.50 $\pm$ 0.11	11.65 $\pm$ 0.07	0.15 $\pm$ 0.04	11.3 $\pm$ 0.07
BC800	4.27 $\pm$ 0.12	11.49 $\pm$ 0.05	11.72 $\pm$ 0.02	0.23 $\pm$ 0.07	11.3 $\pm$ 0.06

**Fig. 5.** Effect of pyrolysis temperature on (a) total acidity/basicity and (b) surface acidic functional groups.**Fig. 6.** XRD (a) and FTIR (b) spectra of feedstock and the produced date palm BCs.

as soluble form or converting into insoluble inorganic compounds by forming new minerals.

3.6. Biochars analysis using XRD, FTIR, TG and SEM

The XRD spectral analysis of the date palm biochar pyrolyzed at 300–800 °C showed different peaks (Fig. 6a), confirming presence of diverse inorganic materials and formation of mineral crystals [10,34]. In the feedstock samples, the two peaks at 11.6 (7.63 Å) and 21.48 (4.14 Å) were identified, suggesting the presence of an

organic mineral mellite ($\text{Al}_2[\text{C}_6(\text{COO})_6] \cdot 16\text{H}_2\text{O}$). In biochar samples, mellite was lost during pyrolysis, while other minerals such as sylvite (KCl), calcite (CaCO_3) and periclase (MgO) depending on pyrolysis temperature were identified. The BC300 mainly contained the mineral calcite (3.03 and 2.82 Å), and sylvite (3.12 and 2.22 Å). With increasing pyrolysis temperature, an additional peak of periclase (MgO) at 2.10 Å was also observed. Furthermore, intensity of calcite peak (3.03 Å) for BC800 became much lower than those of BC500–BC700; meanwhile the peak intensity of 2.10 Å (periclase) was higher.

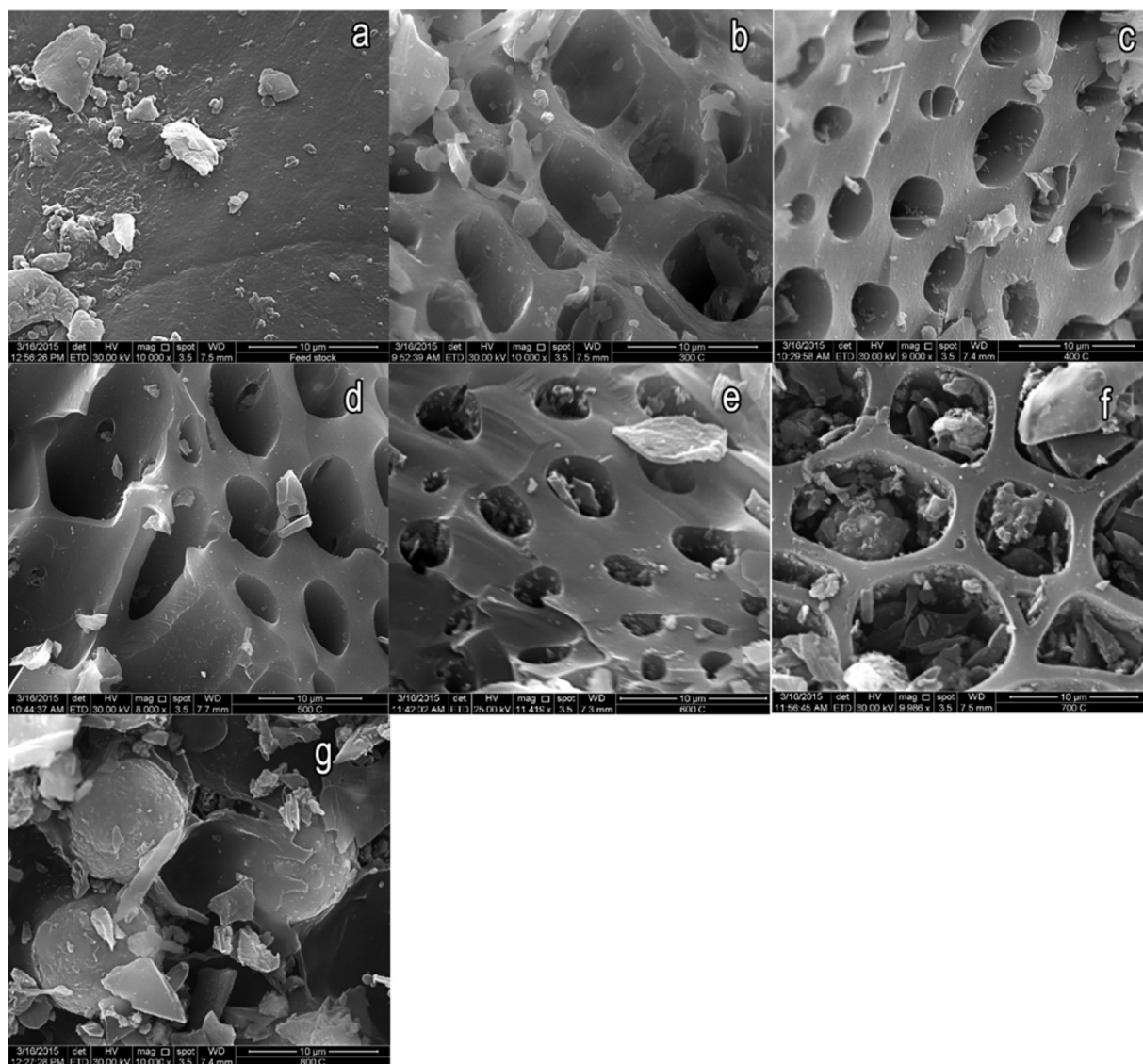


Fig. 7. SEM images of feedstock (a) and biochars pyrolyzed at different temperature of 300 (b), 400 (c), 500 (d), 600 (e), 700 (f) and 800 (g) °C.

The FTIR spectra show that the functional groups of the biochars changed obviously during pyrolytic process (Fig. 6b). The feedstock spectrum is dominated by hydrogen bonded —OH stretching at 3409 cm^{-1} indicating the presence of bonded water and other volatile functional groups that tended to decrease in biochar samples [5]. The appeared aliphatic C—H stretch (2855 and 2920 cm^{-1}) in the feedstock suggests presence of hemicellulose and cellulose, which are reduced in produced BC300–400 and completely eliminated with increasing charring temperature $>500^\circ\text{C}$. This suggests the removal of polar functional groups from biochars with increasing pyrolysis temperature. Moreover, the intense broad band at 1755 cm^{-1} detected only in feedstock spectrum is connected to C=O stretching arising from groups such as quinone, lactone and carboxylic acids, attributing to hemicellulose. Degradation of hemicelluloses is evident with pyrolysis, which is associated with the reduction or disappearance of the 1755 cm^{-1} band in biochar samples. Generally, the carboxylic acids could also be indicated by the band of —COOH at 1600 cm^{-1} [5], which tended to decline with the increase of pyrolysis temperature. Chun et al. [35] found that the amount of acidic groups of —COOH reduced with increased pyrolysis temperature and even disappeared at high temperature. Additionally, the intense band around 1600 cm^{-1} may also be

due to the aromatic C=O and C=C [10]. The band at 1093 cm^{-1} attributed to C—O—C stretching vibrations of polysaccharides. The peak at wave number of 1430 cm^{-1} could be associated with O—H bonds (aliphatic and aromatic groups). In the infrared spectra of the biochars pyrolyzed at $400\text{--}600^\circ\text{C}$, the intensity of this peak is more pronounced. However, the amount of O—H bonds reduced or completely eliminated at highest pyrolysis temperature of 800°C , suggesting a complete loss of OH containing aliphatic compounds. As shown by the infrared spectra, the charring temperature modifies the functional groups, and thus resulting in dehydration of cellulosic and ligneous contents as well as the decrease of aliphatic C groups. The aromatic functional units in biochar samples were condensed. Additionally, the biochars produced at low pyrolysis temperature do possess some functional properties of their feedstock.

Fig. S2 shows the TG curves for the feedstock and produced biochar samples. All the investigated samples of feedstock and biochars show mass loss peaks below 100°C , explaining by the loss of water. Feedstock samples showed higher water content of 5.90% than those of biochars (0.87–2.2%). Generally, with increasing charring pyrolysis temperature, the biochars samples showed little sorbed water, indicating a transformation of a hydrophilic

substance containing OH groups into a hydrophobic material dominated by aromatic functionalities [36]. It has been reported that pyrolysis temperature is a key factor in controlling biochars' thermal stability [25]. In this context, our results showed that as the pyrolysis temperature increased, as the better thermal stability of the biochar is presented. The weight loss was recorded during the process at around 222 °C, 260 °C, 317 °C, 374 °C, 370 °C, 396 °C and 402 °C for feedstock and biochars produced at 300 °C, 400 °C, 500 °C, 600 °C, 700 °C and 800 °C, respectively. The weight loss could be explained by the degradation, and carbon probably converted to CO₂, CO and CH₄. Generally, feedstock and 300 °C biochar showed a different trend with 400–800 °C biochars on the TGA curves. Above 907 °C and 1042 °C, degradation for feedstock and 300 °C biochar is completed and the curves became stable. Lower pyrolysis biochar (BC300) is less thermally stable than the higher pyrolysis biochars (BC400–800), suggesting that BC300 was not completely carbonized.

Fig. 7 shows the SEM analyses of feedstock and biochars pyrolyzed at different temperatures. Surface structures of biochar samples showed porous surfaces, caused by organic materials volatilization. Appearance of deep channels and pores in biochars became more prominent with increasing pyrolysis temperature.

3.7. Implications for environmental and agronomic management

Biochars produced from carbonization of organic wastes have been known to sequester C in soils [1,37]. However, long-term C sequestration potential depends largely on the biochar's stability dependent on production conditions including pyrolysis temperature [11,38]. Based on the results, the date palm derived biochars at pyrolysis temperature ≥ 500 °C with a volatile matter less than 10% and O/C of 0.02–0.05, may exhibit a high C sequestration potential. In this context, it has been speculated that biochars produced at high temperature (>500 °C) could be more resistant to mineralization through biological processes than biochars pyrolyzed at lower temperature (<500 °C), thus becoming efficient technique in mitigating greenhouse gas emission into the environment. Additionally, high pyrolysis temperature biochars have great ameliorating effects on acidic soils [39]. Yuan et al. [5] reported that the improvement effects of biochar on acid soils are not only dependent upon its alkalinity but also are dependent upon its alkali forms. On the contrary, applying high pyrolysis biochars to arid soils with high alkalinity may be critical of concern due to its high pH. Our results suggest that the date palm biochars produced at the low pyrolysis temperature (300–400 °C) that are partially carbonized and have relatively high organic functional groups and lower alkalinity may improve the fertility of arid soils more than those pyrolyzed at high-temperature (700 and 800 °C), inducing nutrient exchange sites as well as enhancing soil cation exchange capacity.

4. Conclusions

Pyrolysis temperature greatly affected the date palm derived biochar characteristics in relation to its elemental composition and surface chemistry. Biochars produced at ≥ 500 °C possessing $<10\%$ volatile matter and 0.02–0.05 molar O/C ratio are more suitable for C sequestration. Nevertheless, low temperature biochars (<500 °C) possessing some properties of their feedstock and having more functional groups as well as relatively low pH values may be more suitable for improving the fertility of high pH soils in arid regions. Our results suggest that the biochars derived from date palm waste may represent potential alternative materials for agronomic or environmental management.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research, King Saud University for funding this work through the international research group project IRG-14-02.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jaap.2015.08.016>.

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